DEVELOPMENT OF ASYMMETRIC POLYETHERSULFONE (PES) MIXED MATRIX MEMBRANE FOR O_2/N_2 SEPARATION

NURUL FARHANAH BINTI CHE BAHAR

A thesis submitted in fulfillment of the requirements for the award of the Degree of Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

DECEMBER 2010

ABSTRACT

The latest rising of polymer-based organic-inorganic composite membrane materials known as mixed matrix membranes (MMMs), have potentially to combine the easy processability of organic polymers with the excellent gas separation properties of inorganic molecular sieve material. In this study, the development of mixed matrix membranes for oxygen/nitrogen (O_2/N_2) separation by manipulating the different types of zeolite was studied in order to identify the best composition of zeolite. Three types of zeolite were used are 4A, 5A and 13X. To enhance the adhesion of zeolite with polymer matrix and also to modify the surfaces of inorganic material, 3-aminopropyl-trimethoxysilane (APTMOS) was introduced to treat the zeolite prior to dope solution preparation. The polymer solution consists of 30 wt% of polyethersulfone (PES) as polymer, 60 wt% of n-methyl-pyrrolidone (NMP) as solvent, 5 wt% of distilled water as non solvent and 5 wt% of different types of zeolite. Asymmetric flat sheet mixed matrix membranes were fabricated using manually casting through dry/wet phase inversion process. Membrane produce was coated with polydimethylsiloxane (PDMS) to produce defects-free membrane. Then, the membrane was tested with the pure oxygen (O_2) gases and nitrogen (N_2) gases by using the permeation test unit with the feed pressure range between 1 to 5 bars. From the pure gas permeation test result, it shows that the MMMs incorporation with zeolite 4A produce the highest selectivity, which is 3.2 and the lowest selectivity can be achieved using zeolite 13X and the selectivity was 1.7 at the optimum pressure of 2 bars. The differences of selectivity value between difference zeolite are because of the pore size of the zeolite. The morphology of prepared membrane had been identified by using Scanning Electron Microscope (SEM). As a conclusion, by adding the polymer solution with difference type of zeolite will exhibit difference membrane performance. It is because of difference zeolite have difference pore size. It also proves that, by adding zeolite 4A, the selectivity of O_2/N_2 is increased.

ABSTRAK

Peningkatan terbaru dari polimer berasaskan bahan organik-bukan organik komposit membran dikenali sebagai membran campuran matrik (MMMs) mempunyai potensi untuk menggabungkan proses mudah polimer organik dengan kecemerlangan sifat pengasingan gas oleh bahan bukan organik bertapis. Dalam kajian ini, pembangunan membran campuran matrik untuk pengasingan oksigen/nitrogen (O_2/N_2) dengan cara memanipulasikan jenis zeolit dilakukan untuk mengenalpasti komposisi zeolit terbaik. Tiga jenis zeolit yang digunakan dalam kajian ini adalah 4A, 5A dan 13X. 3-aminopropil-trimetoksisilan (APTMOS) telah diperkenalkan bagi meningkatkan perekatan antara zeolit dengan matrik polimer dan juga telah mengubahsuai permukaan bahan bukan organic. Larutan polimer yang digunakan terdiri daripada 30 % jisim poliethersulfona (PES) sebagai polimer, 60 % jisim n-metil-pyrrolidona (NMP) sebagai pelarut, 5 % jisim air suling sebagai bahan tambah bukan pelarut dan 5 % jisim pelbagai jenis zeolit. Asimetrik kepingan rata membran campuran matrik dihasilkan secara manual dengan menggunakan proses fasa balikan kering/basah. Membran yang dihasilkan akan disaluti dengan polidimetilsiloxana (PDMS) untuk menghasilkan membran yang tidak mempunyai kecatatan. Selepas itu, membran tersebut akan diuji dengan gas oksigen asli (O_2) dan juga gas nitrogen (N_2) dengan menggunakan mesin penguji kadar penembusan dengan menggunakan tekanan diantara 1 hingga 5 bar. Keputusan kajian kadar penembusan gas asli menunjukkan bahawa penggabungan membran campuran matrik dengan zeolit 4A menghasilkan kadar pemilihan yang tertinggi iaitu 3.2 manakala kadar pemilihan yang paling rendah telah dicapai melalui penggabungan membran campuran matrik dengan zeolit 13X yang menghasilkan kadar pemilihan sebanyak 1.7 pada tekanan yang maksimum iaitu 2 bar. Perbezaan antara nilai kadar pemilihan antara zeolit adalah kerana saiz liang zeolit. Morfologi membran yang dihasilkan dikenalpasti dengan menggunakan Mikroskop Pengimbas Elektron (SEM). Kesimpulannya, dengan menggabungkan larutan polimer dengan jenis zeolit yang berbeza, prestasi yang dihasilkan oleh membran adalah berbeza kerana zeolit yang digunakan mempunyai saiz liang yang berbeza dan ia juga menunjukkan bahawa dengan penambahan zeolit 4A, kadar pemilihan dan kadar pengasingan adalah meningkat.

TABLE OF CONTENTS

CHAPTER 3 METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

P_{eff}	Effective permeability
$\emptyset$	Volume fraction of the dispersed phase
α_{eff}	Effective selectivity of mixed matrix membrane
P_{rel}	Permeability ratio of continuous phase to dispersed phase
P	Pressure-normalized flux
Q_i	Volumetric flow rate of gas i
l	Membrane skin thickness
A	Effective surface area
ΔP	Pressure difference
$\alpha_{i/j}$	Selectivity

LIST OF ABBREVIATIONS

PES	Polyethersulfone
SEM	Scanning electron microscope
MMMs	Mixed matrix membrane
CMS	Carbon molecular sieve
APDMES	Aminopropyldimethyl silane
PSF	Polysulfone
O_2	Oxygen
N_2	Nitrogen
STP	Standard temperature and pressure
GPU	Gas permeation unit
APTMOS	Aminopropyltrimethoxysilane
NMP	1-methyl-2-pyrrolidone
PI	Polyimide
PDMS	Polydimethylsiloxane

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

The development of membrane has seen a rapid growth in the separation technology during a few decades. According to Mulder (1996), a general definition of a membrane could be a selective barrier between two phases of selective. Membrane can identify as an interphase between the two adjacent phases which is function as a regulating transport of substances between two compartments (Mathias, 2006).

From the point of view for gas separation, it has shown that polymeric membranes are very useful thus, it is providing the economical alternatives to conventional separation processes (Sangil and Eva, 2005). However, according to Robeson (1991), polymeric membranes have a limitation in the application of gas separation due to the transaction between permeability and selectivity as shown in upper bound curves.

To increase the gas separation membranes performance, recent work has concentrate on the fabrication of polymer membranes by doing some modifications in the physical and chemical structures of polymer films to enhance better separation quality (Spillman, 1990). According to previous researchers, the incorporation of various inorganic materials such as zeolites or carbon molecular sieve into polymer membrane has been applied (Mahajan and Koros, 2000; Mahajan and Koros, 2002; Kulprathipanja and Neuzil, 1988). The latest emerging polymer-based organic-inorganic composite membrane material may potentially surpass the "upper bound" limit (Vu *et al.*, 2003).

In recent times, many researchers have focused on novel polymer-zeolite mixed matrix membrane to overcome the limitations for the reason that the interaction of materials in the matrix membrane and structure-selective catalytic properties of zeolite can support the perselective separations (Murat *et al.*, 1994).

According to previous researcher (Duval *et al.*, 1993), a very uprising effect in the separation oxygen/nitrogen was observed. By blending the poorly selective rubbery polymers with polydimethylsiloxane (PDMS) with silicalite-1 as zeolite, it has shown an increasingly in the ideal selectivity for oxygen. From the results obtained, it has shown that there is an improvement in performance of permeability oxygen and nitrogen for PDMS membranes with zeolite. The permeability of oxygen and nitrogen for PDMS membrane with zeolite are 1370 barrer and 521 barrer while for PDMS membrane without zeolite is 606 barrer and 289 barrer. There was also having improvement in the selectivity performance of oxygen/nitrogen. For PDMS membrane with zeolite, the selectivity of oxygen/nitrogen is 26 while for PDMS membrane without zeolite is 21. Therefore, from the result obtained, it has shown that the hybrid of mixed matrix membrane have give enhancement on permeability for gas separation compared to using conventional polymer membrane.

Thus, as conclusion the suit combination of polymer membrane with adsorbent such as zeolite can give the improvement on mixed matrix membrane. Therefore, it is expected to provide the superior separation performance that suitable for gas separation application.

1.2 PROBLEM STATEMENT

The different types of zeolite used in mixed matrix membrane played an important role in morphology and separation performance. Nowadays, the challenge face by current application of gas separation membrane is to seek out for a higher selectivity and permeability. By blending the zeolite in the polymer solution, it shows that the permeability and selectivity for gas separation have higher improvement. Spillman (1990) has studied in the case pervaporation of ethanol/water mixture using silicon rubber membrane and have found that both ethanol selectivity and permeability were enhanced by the incorporating of silicalite-1 known as zeolite into the polymer membrane. However, the study is limited for one type of zeolite. Therefore, this study is focus on the development of high performance mixed matrix membranes for gas separation by using various types of zeolite to provide enhancement of selectivity and permeability of gas separation. In order to achieve higher performance of polymer membrane for gas separation, the high quality of membrane should use. Hence, it is essential to blend the polymer membrane with zeolite to ensure the permeability and selectivity of gas separation will be increased.

1.3 OBJECTIVE OF STUDY

Based on the research background and problem statement described in the previous section, the following are the objectives of this research:

1. To develop an asymmetric polyethersulfone (PES) mixed matrix membrane for oxygen/nitrogen (O_2/N_2) separation.
2. To study the effect of different types of zeolite in casting solution on the gas separation performance.

1.4 SCOPES OF RESEARCH

In order to accomplish the above mentioned objectives, the following scopes were drawn:

1. Developing new types of membrane by applying differences type of zeolite to fabricate asymmetric polyethersulfone (PES) membrane for gas separation .
2. Characterization of the developed uncoated and coated membrane using pure N_2 and O_2 gases.
3. Study the morphology of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).

1.5 RATIONALE AND SIGNIFICANT

It has been shown that, from the point of view of gas permeation, gas separation through a membrane has been hoped to be an environmentally begin and simple process. Membrane separation by polymer membrane is a proven technology and has been found in wide range of industrial applications. Gas separation processes require a membrane with high permeability and selectivity. Traditionally, there has been a trade-off between selectivity and permeability. It is because of “upper bound” limit, which a high selectivity membranes tend to exhibits less permeability and vice versa.

Thus, to improve the gas separation characteristics is to incorporate specific adsorbent such as zeolites into the polymeric matrix. A mixed matrix material with inorganic zeolites or carbon molecular sieves will cause the excellent gas separation properties embedded into the matrix of a polymer. By doing some research on the development of high performance mixed matrix membrane, with the inclusion of different types of zeolite as an adsorbent, it will have the potential to achieve the high selectivity without decrease the permeability of gas. For that reason, we can attain a better gas separation.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE SEPARATION TECHNOLOGY

The process industries produce a wide variety of chemicals and components which present the manufacturer with a need for separation, concentration and purification of range materials. In the past decade, the simple concept of separation has been introduced such as a membrane to improve or replace the technique of distillation, adsorption, extraction, crystallization and so on (Baker, 2000).

Membrane separation process has attained an important position in chemical technology presently. It has emerging a rapid growth during the few past decades and also was used in a broad range of application. Generally, membrane is a permeable or semi-permeable phase, commonly a thin polymeric solid which is limited to the motion of certain species. This phase is important barrier between the feed stream for separation and one product stream. The relative transport rate of various species is controlled by membrane through itself (Baker, 1991).

There are many significant capability of membrane technology. The improvement capability of membrane appliance will give a much deeper impact on many features of lives in the future. Membranes have significantly different structures. However, they have the common characteristics of selective transports to different component in feed. Membranes may be homogenous or heterogenous, symmetrical or asymmetrical and porous or non-porous. They also can be organic or inorganic, liquid or solid (Mulder, 1996).

2.2 MEMBRANE HISTORY AND CURRENT STATUS

2.2.1 History of Membrane Technologies

The development of membrane process has become an emerging technology. It has been starting growth since early 1748 by Abbe Nolet. Then, it has seen a very rapid progress of this technology by other researchers. Table 2.1 clarify the history of membrane development.

Table 2.1: History of membrane technologies

Year	Name of inventor	Inventor
1748	Abbe Nolet	• The word ‘osmosis’ is coined to describe the permeation of water through diaphragm.
Membranes had no industrial or commercial uses in the 19th and early 20th centuries. It only were used as laboratory tools to develop physical and chemical theories. Traube and Pfeffer were made the measurements of solution osmotic pressure with membranes.		
1887	Van’t Hoff	• Develop his limit law which the measurements of solution osmotic pressure made with membranes to give the explaination about the behavior of ideal dilute solutions. • Lead directly to Van’t Hoff equation.
	Maxwell et al	• Used the concept of a perfectly selective semipermeable membrane in developing the kinetic theory of gases.
1907	Bechhold	• Develop a technique to prepare nitrocellulose membranes of graded pore size which determined by a bubble test.
1903	Elford, Zsigmondy and Bachmann and Ferry	• Microporous collodion membrane was commercially available.
During the next 20 years, the early microfiltration membrane technology was spread out to other polymers such as cellulose acetate. The first significant application of membrane is in the testing of drinking water.		
1960	Loeb-Sourirajan	• Development of membrane industrial process for making defect-free, high flux, anisotropic reverse osmosis membranes. • These membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable

		microporous support which provides the mechanical strength. • The flux of the reverse osmosis membrane was 10 times higher than any of membrane.
1966	Alex-Zaffaroni	a) Found many company were used membrane in the pharmaceutical industry to improve the efficiency and safety of drug delivery.
1980	Monsanto Prism ®	b) Develop membrane for hydrogen separation.
Few years later	Dow	c) Produced systems to separate nitrogen from air.
	Cynara and Separex	d) Produced systems to separate carbon dioxide from natural gas.

Source: Baker (2000)

In the period from 1960 to 1980, the status of membrane technology has seen rapidly growth. It is begun with the original Loeb-Sourirajan technique. There were several membrane formation processes. It was include the interfacial polymerization and multilayer composite casting and coating for making high performance of membrane (Baker, 2000).

2.2.2 Current Status of Membrane Technologies

Membrane technology has more lately been applied commercially to separate individual components. The uses of membrane are varied which it can be locate in different ways. It can be used for separation of mixtures of gases and vapors, miscible liquids (organic mixture and aqueous/organic mixtures) and solid/liquid and liquid/liquid dispersion s and dissolved solids and solutes from liquids (Mulder, 1996). The current status of membrane technologies in industrial application are shown in Table 2.2.

Table 2.2: Current status of membrane technologies

Category	**Process**	**Status**
Developed industrial membrane separation	Microfiltration, ultrafiltration, reverse osmosis, electrodilysis	Well-established unit operations. No major break-throughs seem imminent.
Developing industrial membrane separation technologies	Gas separation, pervaporation	A number of plants have been installed. Market size and number of applications served expanding.
To-be-developed industrial membrane separation technologies	Carrier-facilitated transport, membrane contactors, piezodialysis	Major problems remain to be solved before industrial systems will be installed on a large scale.
Medical application of membranes	Artificial kidneys, artificial lungs, controlled drug delivery	Well-established processes. Still the focus of research to improve performance.

Source: Baker (2000)

2.3 MEMBRANE CLASSIFICATION

Membrane can be classified according to their structure and function. A comprehensive representation of the relationships between pore diameters, membrane separation process and penetrant size is shown in Figure 2.1 (Mulder, 1996).

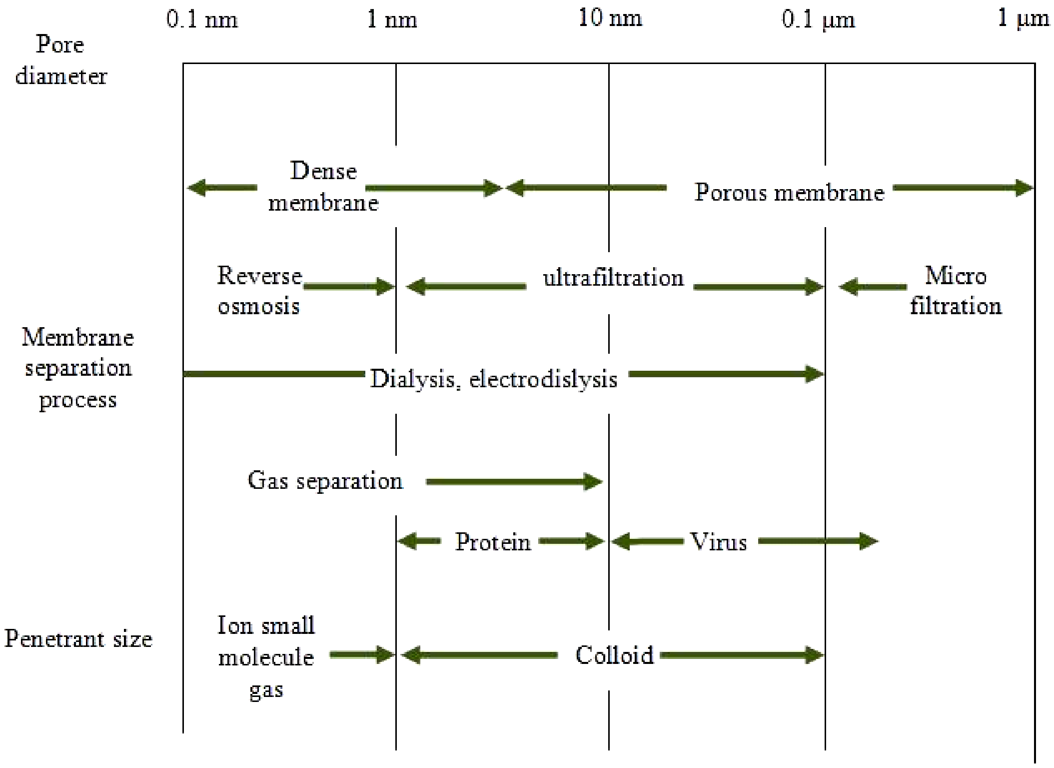


Figure 2.1: Relationship between pore diameter, membrane separation process and penetrant size

Source: Mulder (1996)

According to Mulder (1996), membranes may be homogenous or heterogenous which means the classifying homogenity of a membrane phase. The homogenous membranes specify a homogenous membrane structure parallel and perpendicular to the membrane surface while heterogenous membranes means it have a heterogenous structure. Usually, the degree of heterogenity for various types of membrane is different. Membranes may be also symmetrical or asymmetrical, porous and non porous. They also can be organic or inorganic and liquid or solid. The membrane types and its applications are shown in Table 2.3 below.

Table 2.3: Major application of membrane process

Membrane separation	**Membrane type**	**Driving force**	**Applications**
Microfiltration	Symmetric microporous	Hydrostatic pressure	Clarification, steril filtration, purification of fluids in semiconductor manufacturing industry, clarification and biological stabilization in the beverage industry, sterilization (in the food and pharmaceutical industries) analysis
Ultrafiltration	Asymmetric microporous	Hydrostatic pressure	Separation of macromolecular solutions, electrodialysis pretreatment, electrophoretic paint, cheese whey treatment, juice clarification, recovery of textile sizing agents, wine clarification, separation of oil/water emulsion, concentration of latex emulsion from wastewater, dewaxing, deasphalting, egg-white preconcentration, kaolin concentration, water treatment, affinity membranes, reverse osmosis pretreatment
Nanofiltration	Asymmetric microporous	Hydrostatic pressure	Separation of small organic compounds and selected salts from solutions, water treatment, product and chemical recovery, concentration/dewatering, fractionation of monovalent and diavalent cations, water softening
Hyperfiltration	Asymmetric, composite with homogenous skin	Hydrostatic pressure	Separation of microsolutes and salts from solutions
Gas permeation	Asymmetric or composite, homogenous porous polymer	Hydrostatic pressure, concentration gradient	Separation of gas mixture, Hydrogen recovery (Synthesis gas ratio adjustment (H2/CO), H_2 recovery from hydroprocessing purge streams, H_2 recovery from ammonia plant purge streams and other petro chemical plant streams), oxygen/nitrogen separation, helium recovery, removal of acid gases from light hydrocarbons, biogas processing, separation of organic vapors from air

Table 2.3: (Continued)

Dialysis	Symmetric microporous	Concentration gradient	Separation of microsolutes and salts from macromolecular solutions, hemofiltration and hemodiafiltration, donnan dialysis, alcohol reduction of beverages
Pervaporation	Asymmetric, composite	Concnentration gradient, vapor pressure	Separation of mixtures of volatile liquids, removal of organics from water, water removal from liquid organics, organic/organic separation
Vapour permeation	Composite	Concentration gradient	Separation of volatile vapours and gases Removal of organics from air
Membrane distillation	Microporous	Temperature	Separation of water from non-volatile solutes
Electrodialysis	Ion-exchange, homogenous or microporous polymer	Electrical potential	Separation of ions from water and non-ionic solutes, desalination of brackish water, production of table salt, waste water treatment, concentration of RO brines, applications in the chemical, food and drug industries
Electro-osmosis	Microporous charged membrane	Electrical potential	Dewatering of solutions of suspended solids, sea water and brackish water desalination, waste water treatment (industrial and municipal, pulp and paper. Textile waste water), production of boiler quality water for steam generation, petroleum industry, recovery of plating chemicals from wastewaters and process waters in the electroplating chemicals from wastewaters and metal-finishing industry
Electrophoresis	Microfiltration membranes	Electrical potential, hydrostatic pressure	Separation of water and ions from colloidal solutions
Liquid membranes	Microporous, liquid carrier	Concentration, reaction	Separation of ions and solutes from aqueous solutions

Source: Khulbe *et al.* (2008)

2.4 ADVANTAGES OF MEMBRANE TECHNOLOGY

Membranes separation process has become one of the vital technologies for industrial application. It has seen in many industrial applications since it has many benefits. Below are the following advantages of membrane technologies.

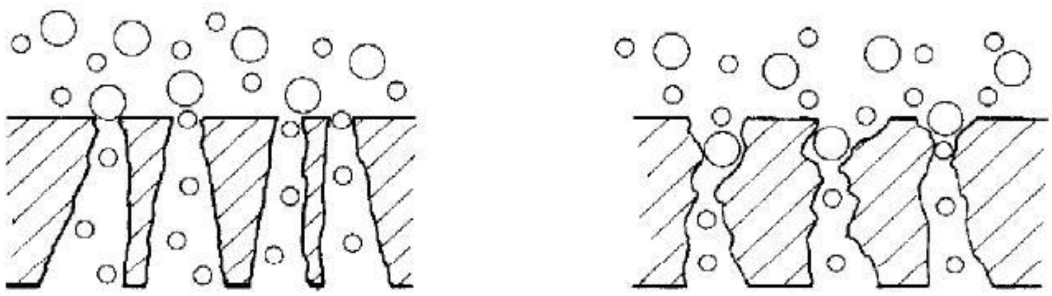
a) Membrane separation process offer the low capital cost and have cost effectiveness. It is because membrane used low operating cost and low energy consumption.
b) The operation of membrane process used low energy consumption. It is because during the separation process there is no phase change. So, the energy used is low and at the same time we can save the energy.
c) The membrane process is easy to operate. Membrane separation processes do not required a complex machine. Its only need the simple, easy to operate and compact equipment.
d) Membrane separation has space efficiency because of its shape, molecular size and also charge. The porous structure of the membrane can make the membrane will have the larger space effectiveness.
e) Keep the product quality. The membrane separation can be operate at room temperature. So, it is not required to increase and decrease the temperature during the separation process.
f) No additional waste product. Membrane is a clean technology because it is not produce the unwanted product.

2.5 TYPES OF MEMBRANES STRUCTURE

Membranes can be classified according to their morphology. Generally, the functioning of membrane will depend on its structure since this configuration determines the mechanism of separation and thus application. There have two types of structure that usually found in membrane. They are either homogenous or symmetric membrane or heterogenous or asymmetric membrane. This study is focusing only for asymmetric membrane. Table 2.4 below shown the differences between symmetric and asymmetric sructure of membrane and Figure 2.2. shows the schematic diagram of the structure of membrane.

Table 2.4: Differences of membrane structure

Asymmetric membrane (heterogenous)	**Symmetric membrane (homogenous)**
1) Have three basic structures 2) Integral skinned asymmetric membrane with a porous skin layer 3) Integral skinned asymmetric membrane with a dense skin layer 4) Thin film composite membranes	1) The structure is same across the thickness of membrane 2) Can be porous or dense uniform structure



(a) Asymmetric membrane (b) Symmetric membrane

Figure 2.2: Schematic diagram of the membrane behavior of (a) asymmetric membrane and (b) symmetric membrane

2.6 ASYMMETRIC MEMBRANES

Most membranes that are used in industrial have an asymmetric structure. Asymmetric membrane consists of two structurally distinct layers, one of which is a thin, dense, selective skin or barrier layer and the other a thick, porous matrix layer whose chief function is to provide a physical support for the thin skin. The skin layer performs the separation with a high flux because it is thin and with a high selectivity due to its high density. The porous sublayer provides the mechanical strength that the gases permeate without resistance (Baker, 1991). Figure 2.3 shows asymmetric membranes that have developed by Loeb Sourirajan. The membranes consist of an extremely thin and dense surface layer (0.1μm to 1 μm) supported on a much thicker porous sublayer (100 μm to 200 μm of the same material). (Guang-Li, 1993; Ismail and